Flash vacuum pyrolysis of stabilised phosphorus ylides. Part 13.[1] Extrusion of Ph₃P from sulfinyl ylides and reactivity of the resulting sulfinyl carbenes
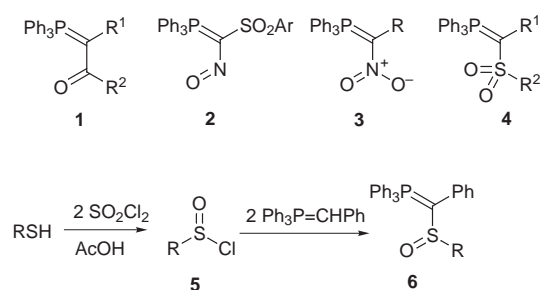
R. Alan Aitken,* Martin J. Drysdale and Bruce M. Ryan

School of Chemistry, University of St. Andrews, North Haugh, St. Andrews, Fife, UK KY16 9ST

Six α-sulfinyl phosphorus ylides **6** have been prepared and are found upon flash vacuum pyrolysis at 500 °C to undergo mainly extrusion of Ph₃P to give thioesters, presumably by 1,2-oxygen transfer in the initially formed sulfinyl carbenes; for α-arylsulfinyl ylides loss of Ph₃PO to give additional products is also observed.

Although the thermal extrusion of Ph₃PO from α-acylphosphonium ylides **1** to give alkynes is well established,[2] the corresponding reaction of ylides bearing other oxygen containing functional groups on the α-position has been little investigated. Sulfonyl cyanides have been prepared by spontaneous extrusion from α-nitroso ylides **2** at −40 °C,[3] and there is evidence for extrusion of Ph₃PO from α-nitro ylides **3** to give nitrile oxides.[4] In Part 12 of this series,[1] we reported that sulfonyl ylides **4** undergo loss of Ph₃P rather than Ph₃PO upon flash vacuum pyrolysis (FVP) to give products derived from sulfonyl carbenes. We now report the preparation and pyrolytic behaviour of representative α-sulfinyl ylides **6**.[5]

For the alkanesulfinyl ylides **6a–c**, FVP at 500 °C and 10⁻² Torr (contact time *ca.* 10⁻² s) resulted mainly in extrusion of Ph₃P to give the thioesters **7** (Table 1). Since spectroscopic data for the thioester **7c** have apparently not been reported before, an authentic sample of this was prepared for comparison. The reaction can be explained by a 1,2-oxygen transfer in the initially formed sulfinyl carbenes *via* the zwitterionic oxathiirane intermediate **14** (Scheme 1). Sulfinyl carbenes are a little known
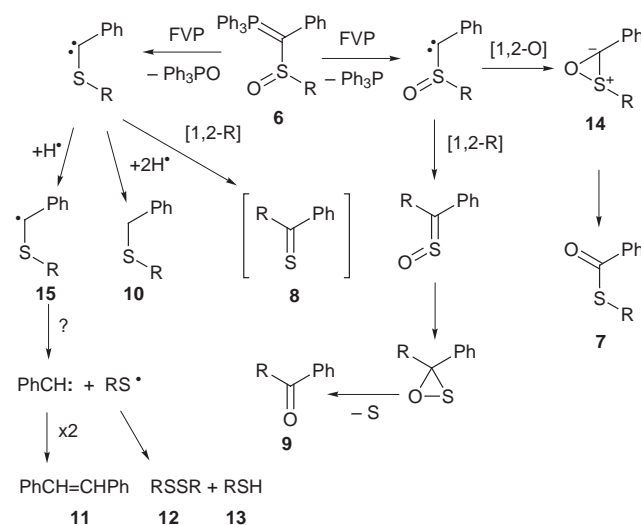
Scheme 1

class of reactive intermediates,[9] but this type of oxygen transfer has been observed before in two cases.[10,11] The analogous rearrangement of nitro carbenes to acylnitroso compounds has been described,[12] as has 1,4-O-transfer from sulfur in an *N*-sulfonylimidoyl carbene to give the sulfinylimidoyl ketone.[13]

For **6a,b** there was also some loss of Ph₃PO to give other minor products, and for the ylides **6c–f** competing processes were more important, although **7** was still formed in each case. Since **7e,f** appear to be previously unknown, authentic samples were prepared by an alternative route and characterised. To confirm that these compounds were stable under the pyrolysis conditions and would not give rise to any secondary products, they were each subjected to FVP at 500 °C but were recovered unchanged. In Table 1 the balance of the phosphorus products is accounted for in each case by Ph₃PS, presumably formed by interaction of Ph₃P with sulfur containing products. The most obvious feature for **6d–f** was the production of an intense dark

Results and discussion

The sulfinyl ylides are little known and there were, until recently, only two reports of their synthesis,[6] both involving additional stabilisation by an ester group. Synthesis of the first examples without additional stabilisation, a range of (alkylsulfinylmethylene)diphenylmethylphosphoranes, was recently described by reaction of a lithium phosphonium diylide with sulfinate esters.[7] The required ylides **6** were readily formed in low to moderate yield (Table 1) in analogy to the acyl ylides **1**, by reaction of Ph₃P=CHPh (2 equiv.) with sulfinyl chlorides **5**. The sulfinyl chlorides which are notoriously unstable and difficult to purify were used directly as obtained from the improved method[8] involving treatment of RSH with 2 equiv. SO₂Cl₂ and 1 equiv. AcOH. The ylides were easily recognised from the characteristic doublet ($^1J_{P–C}$ 122–128 Hz) due to the ylide carbon in their ¹³C NMR spectra (see Table 2). The compounds proved to be rather unstable and difficult to purify and the low yield in the case of **6c** meant that correct analytical data could not be obtained, although the consistent pattern of ¹³C NMR data across the series leaves little doubt as to its identity. Significantly the majority of the compounds showed a peak for M⁺ − O as the highest signal in the mass spectrum.

Table 1 Formation of sulfinyl ylides **6** and results of their pyrolysis at 500 °C

	R	Yield of **6** (%)	δ_P	Products from FVP of **6** (%)							
				Ph$_3$P	Ph$_3$PO	7	9	10	11	12	13
a	Et	24	+19.7	80	13	53	—	—	—	—	—
b	Pr^i	33	+20.2	84	9	37	—	—	—	—	—
c	CH$_2$Ph	4	+18.7	50	40	30	—	2	10	—	—
d	Ph	29	+20.4	64	32	20	—	4	10	10	8
e	4-Me-C$_6$H$_4$	45	+20.2	82	15	25	5	—	—	6	20
f	4-Cl-C$_6$H$_4$	31	+19.7	27	67	9	18	7	7	17	25

Table 2 ^{13}C NMR Spectra of ylides **6**, δ_C ($J_{P–C}$)

	R	P=C	P–Phenyl				P=C–Ph signals				R signals
			C-1	C-2	C-3	C-4	C-1	C-2	C-3	C-4	
a	Et	47.9 (126)	127.7 (86)	134.2 (10)	128.6 (12)	131.9 (2)	137.1 (14)	131.5 (6)	127.8	124.0	45.4 (12), 10.1
b	Pr^i	47.2 (123)	127.5 (89)	134.3 (10)	128.6 (12)	132.0 (2)	137.3 (11)	131.9 (5)	127.7	124.1	49.6 (12), 19.0, 18.7
c	CH$_2$Ph	47.1 (128)	127.0 (90)	134.0 (10)	128.6 (12)	132.1 (<2)	138.3 (12)	131.9 (5)	127.9	123.5	56.3 (12), 133.2, 130.5 (2C), 128.4 (2C), 127.0
d	Ph	52.2 (122)	126.8 (89)	134.3 (10)	128.8 (12)	132.4 (2)	137.2 (12)	129.7 (6)	127.3	122.7	147.7 (16), 127.8 (2C), 126.3 (2C), 128.6
e	4-Me-C$_6$H$_4$	52.1 (125)	128.0 (78)	134.3 (10)	128.8 (12)	132.3 (<2)	137.4 (12)	132.0 (7)	127.3	122.6	144.6 (16), 137.7, 128.7 (2C), 126.3 (2C), 21.1

blue colour in the cold trap which faded rapidly upon warming. This is attributed to the thioketones **8** although they were only present in trace quantities and could not be detected spectroscopically despite authentic samples being prepared for comparison. The formation of these products may be due to rearrangement of the sulfenyl carbenes resulting from Ph$_3$PO extrusion and the failure to detect them spectroscopically is explained by their rapid reaction with Ph$_3$P in solution to give Ph$_3$PS (δ_P +42.8) as confirmed by a control experiment using **8d**.

A major product for **6e,f** was the ketone **9** which most likely results from rearrangement of the sulfinyl carbene to a sulfine followed by loss of sulfur. A closely related example, dimethyl-vinyl(p-tolylsulfinyl)carbene, has been reported to give the ketone in excellent yield in an analogous way,[14] and the absence of this process for **6a**–**c** probably reflects the poorer migratory aptitude of alkyl vs. aryl groups. In fact there seems to be a fine balance in the reactivity of sulfinyl carbenes between undergoing 1,2-oxygen transfer to give thioesters and the alternative Wolff-type rearrangement to sulfines. While rhodium catalysed reaction of cephalosporin-derived α-diazo sulfoxides results in oxygen transfer,[11] photolysis of the same precursors give the sulfines.[15] In very recent work, Maguire and coworkers have found that rhodium catalysed reaction of cyclic α-diazo sulfoxides also proceeds by way of a sulfine.[16]

The remaining products can be accounted for by alternative reactions of the sulfenyl carbene resulting from extrusion of Ph$_3$PO. The benzyl sulfide **10** is clearly formed by hydrogen atom abstraction, but the formation of stilbene **11** is more difficult to explain. Although the disulfide **12** and thiol **13** may be formed by a variety of radical processes which generate RS˙, it is attractive to speculate that all three products may result as shown from an α-elimination process of radical **15** formed by abstraction of a single hydrogen atom by the sulfenyl carbene, although we are not aware of any precedent for this process. In control experiments, FVP of **10e,f** and **9e,f** at 500 °C established that they are stable under these conditions and do not lead to any secondary products. A further complication is the possibility of disproportionation of **6** in the inlet tube which has been observed for other sulfinyl ylides,[17] and would lead to further products from pyrolysis of sulfenyl and sulfonyl ylides.

Experimental

Melting points were recorded on a Reichert hot-stage microscope and are uncorrected. UV–visible spectra were recorded using a Pye-Unicam SP-800 instrument. Infrared spectra were recorded as Nujol mulls for solids and as thin films for liquids on a Perkin-Elmer 1420 instrument. NMR spectra were obtained for ^{1}H at 300 MHz and for ^{13}C at 75 MHz using a Bruker AM300 instrument, and for ^{31}P at 32 MHz using a Varian CFT 20 instrument. All spectra were run on solutions in CDCl$_3$ with internal Me$_4$Si as reference for ^{1}H and ^{13}C and external 85% H$_3$PO$_4$ as reference for ^{31}P. Chemical shifts are reported in ppm to high frequency of the reference and coupling constants J are in Hz. In the reporting of ^{13}C NMR spectra, 4ry refers to quaternary carbon. Mass spectra were obtained on an AEI/Kratos MS-50 spectrometer using electron impact at 70 eV. GC–MS data were obtained using a Hewlett Packard 5890A chromatograph coupled to a Finnigan Incos mass spectrometer. The column used was a 25 m capillary column HR17 with a phenyl methyl silicone stationary phase. Toluene was dried by storing over sodium wire.

The sulfinyl chlorides **5a**–**f** were prepared according to the literature procedure,[8] by treatment of the corresponding thiols with one equiv. acetic acid and two equiv. sulfuryl chloride at −45 °C.

Preparation of the sulfinyl ylides 6

A suspension of benzyltriphenylphosphonium chloride (10.0 g, 26 mmol) in dry toluene (100 cm^3) was stirred at 0 °C under nitrogen while a solution butyllithium (2.5 M, 10.3 cm^3, 26 mmol) was added. After stirring for 30 min, a solution of the appropriate sulfinyl chloride **5** (13 mmol) in dry toluene (10 cm^3) was added dropwise. After stirring at room temperature for 12 h, the mixture was filtered and the filtrate evaporated. Trituration of the residual oil with ethyl acetate gave the product.

[Ethylsulfinyl(phenyl)methylene]triphenylphosphorane 6a. Reaction as above using ethanesulfinyl chloride gave yellow crystals (24%), mp 169–172 °C (Found: C, 75.4; H, 5.9. C$_{27}$H$_{25}$-OPS requires C, 75.7; H, 5.9%) (HRMS: found M$^+$ − O,

412.1436. $C_{27}H_{25}OPS$ requires $M - O$, 412.1415); ν_{max}/cm^{-1} 1591, 1489, 1436, 1255, 1240, 1101, 1093, 999, 977, 917, 754 and 694; δ_H 7.7–6.9 (20 H, m), 2.86 (2 H, q, J 7) and 1.08 (3 H, t, J 7); δ_C see Table 2; δ_P +19.7; m/z 412 ($M^+ - O$, 5%), 383 (10), 351 (1), 300 (1), 277 (12), 262 (12), 183 (32) and 121 (100).

[Phenyl(isopropylsulfinyl)methylene]triphenylphosphorane 6b. Reaction as above using propane-2-sulfinyl chloride gave yellow crystals (33%), mp 145–148 °C (Found: C, 75.6; H, 5.8. $C_{28}H_{27}$-OPS requires C, 76.0; H, 6.1%) (HRMS: found $M^+ - Pr^i$, 399.0956. $C_{28}H_{27}OPS$ requires $M - Pr^i$, 399.0972); ν_{max}/cm^{-1} 1190, 1114, 1100, 1031, 988, 925, 752, 722 and 697; δ_H 7.7–6.9 (20 H, m), 3.08 (1 H, septet of d, J 7, 2), 1.28 (3 H, dd, J 7, 1) and 1.08 (3 H, d, J 7); δ_C see Table 2; δ_P +20.2; m/z 426 ($M^+ - O$, 1%), 400 (12), 399 (41), 263 (43), 262 (71), 183 (78), 121 (76) and 105 (100).

[Phenylmethylsulfinyl(phenyl)methylene]triphenylphosphorane 6c. Reaction as above using phenylmethanesulfinyl chloride gave yellow crystals (4%), mp 159–161 °C; ν_{max}/cm^{-1} 1255, 1190, 1108, 1000, 934, 758, 720 and 698; δ_H 7.8–6.9 (25 H, m), 4.58 (1 H, half AB pattern of d, J 12, 2) and 4.08 (1 H, half AB pattern, J 12); δ_C see Table 2; δ_P +18.7; m/z (no M^+ at 490) 415 (3%), 400 (4), 398 (20), 382 (12), 351 (8), 294 (5), 292 (4), 277 (8), 262 (57), 228 (6), 183 (100), 121 (96), 105 (90), 91 (78) and 77 (95).

[Phenylsulfinyl(phenyl)methylene]triphenylphosphorane 6d. Reaction as above using benzenesulfinyl chloride gave yellow crystals (29%), mp 172–174 °C (HRMS: found $M^+ - O$, 460.1423. $C_{31}H_{25}OPS$ requires $M - O$, 460.1415); ν_{max}/cm^{-1} (CH_2Cl_2) 1590, 1487, 1440, 1243, 1190, 1102, 1000 and 960; δ_H 7.8–6.7 (25 H, m); δ_C see Table 2; δ_P +20.4; m/z 460 ($M^+ - O$, 2%), 399 (1), 277 (13), 262 (21), 218 (40), 200 (40), 183 (12), 143 (15), 105 (50) and 91 (100).

[4-Methylphenylsulfinyl(phenyl)methylene]triphenylphosphorane 6e. Reaction as above using 4-methylbenzenesulfinyl chloride gave yellow crystals (45%), mp 168–173 °C (Found: C, 78.6; H, 5.5. $C_{32}H_{27}OPS$ requires C, 78.3; H, 5.5%) (HRMS: found $M^+ - O$, 474.1476. $C_{32}H_{27}OPS$ requires $M - O$, 474.1520); ν_{max}/cm^{-1} (CH_2Cl_2) 1590, 1490, 1440, 1243, 1190, 1102, 1000, 928 and 812; δ_H 8.0–6.8 (24 H, m) and 2.28 (3 H, s); δ_C see Table 2; δ_P +20.2; m/z 474 ($M^+ - O$, 0.2%), 394 (0.5), 379 (1), 351 (0.2), 277 (14), 262 (26), 183 (45), 105 (67) and 77 (100).

[4-Chlorophenylsulfinyl(phenyl)methylene]triphenylphosphorane 6f. Reaction as above using 4-chlorobenzenesulfinyl chloride gave yellow crystals (31%), mp 194–196 °C (HRMS: found $M^+ - O$, 494.1020. $C_{31}H_{24}^{35}ClOPS$ requires; $M - O$, 494.1025); ν_{max}/cm^{-1} 1590, 1485, 1440, 1248, 1190, 1100, 1000, 982, 822, 752 and 697; δ_H 7.8–6.8 (24 H, m); δ_C see Table 2; δ_P +19.7; m/z 496 ($^{37}Cl-M^+ - O$, 0.3%), 494 ($^{35}Cl-M^+ - O$, 1), 383 (1), 309 (0.5), 277 (33), 262 (12), 233 (5), 183 (10), 121 (23) and 77 (100).

Flash vacuum pyrolysis of ylides

The apparatus used was as described previously.[18] All pyrolyses were conducted with a furnace temperature of 500 °C and at pressures in the range 10^{-3}–10^{-1} Torr and were complete within 1 h. Under these conditions the contact time in the hot zone was estimated to be ≈10 ms.

In all cases the phosphorus containing products collected at the furnace exit and the more volatile products were recovered from the cold trap. Yields were determined by calibration of the ^1H NMR spectra by adding an accurately weighed quantity of a solvent such as CH_2Cl_2 and comparing integrals, a procedure estimated to be accurate to ±10%.

FVP of the ylide **6a** (110 mg) gave a solid at the furnace exit which was shown by ^{31}P and ^1H NMR and GC–MS to consist of Ph_3P, Ph_3PO and Ph_3PS in a ratio of 80:13:7: Ph_3P; δ_P −5.4; m/z 262 (12%), 183 (45), 152 (16) and 108 (100). Ph_3PO; δ_P +28.6; m/z 277 ($M^+ - H$, 100%), 201 (28), 183 (27) and 152 (10). Ph_3PS; δ_P +43.6; m/z 294 (M^+, 91%), 262 (15), 217 (15) and 183 (100). The liquid in the cold trap was shown to be almost pure S-ethyl thiobenzoate **7a** (53%); δ_H 8.1–7.9 (2 H, m), 7.3–7.5 (3 H, m), 3.08 (2 H, q, J 7) and 1.35 (3 H, t, J 7); δ_C 192.1, 23.4 and 14.8; m/z 166 (M^+, 5%) and 105 (100).

FVP of the ylide **6b** (200 mg) gave a solid at the furnace exit which was shown by ^{31}P and ^1H NMR and GC–MS to consist of Ph_3P, Ph_3PO and Ph_3PS in a ratio of 84:9:7. The liquid in the cold trap was shown to be almost pure S-isopropyl thiobenzoate **7b** (37%); δ_H 8.2–8.0 (2 H, m), 7.7–7.5 (3 H, m), 3.92 (1 H, septet, J 7) and 1.44 (6 H, d, J 7); δ_C 192.1, 137.4, 133.1, 128.5 (2C), 127.1 (2C), 34.7 and 23.1 (2C); m/z 180 (M^+, 5%), 138 (1), 105 (100) and 77 (45).

FVP of the ylide **6c** (105 mg) gave a solid at the furnace exit which was shown by ^{31}P and ^1H NMR and GC–MS to consist of Ph_3P, Ph_3PO and Ph_3PS in a ratio of 50:40:10. The liquid in the cold trap was shown by NMR, GC–MS and comparison with authentic samples to consist of S-benzyl thiobenzoate **7c** (30%); δ_H 7.96 (2 H, m) and 4.32 (2 H, s); m/z 228 (M^+, 5%) and 105 (100) together with smaller quantities of bibenzyl (4%); m/z 182 (M^+, 10%), 91 (100), (Z)-stilbene **11** (2%) and (E)-stilbene **11** (8%); m/z 180 (M^+, 82%) and dibenzyl sulfide **10e** (2%); m/z 214 (M^+, 6%), 123 (22) and 91 (100).

FVP of the ylide **6d** (200 mg) gave a yellow liquid at the furnace exit which was shown by ^{31}P and ^1H NMR and GC–MS to consist of Ph_3P, Ph_3PO and Ph_3PS in a ratio of 64:32:4. The bright blue liquid in the cold trap was shown by NMR, GC–MS and comparison with authentic samples to consist of benzenethiol **13d** (8%); m/z 110 (M^+, 100%), (Z)-stilbene **11** (2%); m/z 180 (M^+, 38%), (E)-stilbene **11** (8%); m/z 180 (M^+, 63%), benzyl phenyl sulfide **10d** (4%); m/z 200 (M^+, 3%), 109 (5) and 91 (100), diphenyl disulfide **12d** (10%); m/z 218 (M^+, 8%), 185 (4), 154 (9) and 109 (100) and S-phenyl thiobenzoate **7d** (20%); m/z 214 (M^+, 1%), 184 (1), 152 (1), 105 (90) and 77 (100).

FVP of the ylide **6e** (110 mg) gave a yellow liquid at the furnace exit which was shown by ^{31}P and ^1H NMR and GC–MS to consist of Ph_3P, Ph_3PO and Ph_3PS in a ratio of 82:15:3. The bright blue liquid in the cold trap was shown by NMR, GC–MS and comparison with authentic samples to consist of benzaldehyde (5%); δ_H 10.0; m/z 106 (M^+, 55%); 4-methylbenzenethiol **13e** (20%); δ_H 3.4 (1 H); m/z 124 (M^+, 42%) and 91 (100), 4-methylbenzophenone **9e** (5%); m/z 196 (M^+, 12%), 119 (100), 105 (37), 91 (54) and 77 (55), S-(4-methylphenyl) thiobenzoate **7e** (25%); δ_H 8.0 (2 H, m) and 2.40 (3 H, s); m/z 228 (M^+, 1%), 123 (5) and 105 (100) and bis(4-methylphenyl) disulfide **12e** (6%); m/z 246 (M^+, 8%), 214 (1), 182 (4) and 123 (66).

FVP of the ylide **6f** (180 mg) gave a yellow liquid at the furnace exit which was shown by ^{31}P and ^1H NMR and GC–MS to consist of Ph_3P, Ph_3PO and Ph_3PS in a ratio of 26:68:6. The bright blue liquid in the cold trap was shown by NMR, GC–MS and comparison with authentic samples to consist of 4-chlorobenzenethiol **13f** (25%); δ_H 3.47 (1 H); m/z 144 (^{35}Cl-M^+, 100%) and 109 (48), (E)-stilbene **11** (7%), 4-chlorobenzophenone **9f** (18%); m/z 216 (^{35}Cl-M^+, 60%), 181 (20), 139 (95), 111 (40) and 105 (100), benzyl 4-chlorophenyl sulfide **10f** (7%); δ_H 4.04 (2 H); m/z 234 (^{35}Cl-M^+, 19%), 143 (8) and 91 (100), S-(4-chlorophenyl) thiobenzoate **7f** (9%); m/z 248 (^{35}Cl-M^+, 4%), 143 (10) and 105 (100) and bis(4-chlorophenyl) disulfide **12f** (17%); m/z 286 ($^{35}Cl_2$-M^+, 30%), 222 (3), 143 (100) and 108 (50).

Preparation of authentic samples of pyrolysis products

Preparation of thiobenzoates 7. A solution of the appropriate thiol (80 mmol) and triethylamine (8.3 g, 82 mmol) in dry toluene (100 cm³) was stirred while a solution of benzoyl chloride

(11.3 g, 82 mmol) in dry toluene (10 cm³) was added dropwise. After 2 h, the mixture was filtered, washed with water, dried and evaporated. Using this method the following compounds were prepared.

S-Benzyl thiobenzoate 7c. From phenylmethanethiol (32%) as a colourless oil which crystallised with time, bp 110 °C (oven temp.) at 2 Torr, mp 34–36 °C (lit.,[19] 39.5 °C); δ_H 8.0–8.2 (2 H, m), 7.2–7.6 (8 H, m) and 4.35 (2 H, s).

S-Phenyl thiobenzoate 7d. From thiophenol (75%) as colourless flakes, mp 50–51 °C (lit.,[20] 56 °C); δ_H 8.0 (2 H, m) and 7.3–7.6 (8 H, m).

S-(4-Methylphenyl) thiobenzoate 7e. From 4-methylthiophenol (45%) as colourless crystals, mp 65 °C (Found: C, 73.7; H, 5.6. $C_{14}H_{12}OS$ requires C, 73.7; H, 5.3%) (HRMS: found M^+, 228.0612. $C_{14}H_{12}OS$ requires M, 228.0609); ν_{max}/cm^{-1} 1670, 1605 and 1590; δ_H 8.02 and 7.18 (4 H, AB pattern, *J* 9), 7.35–7.55 (5 H, m) and 2.34 (3 H, s); δ_C 191.0 (C=O), 140.3 (4ry), 137.3 (4ry), 135.7 (2 C), 134.2, 130.7 (2 C), 129.4 (2 C), 128.1 (2 C), 124.5 (4ry) and 22.0; *m/z* 228 (M^+, 15%), 123 (5), 105 (100), 91 (4) and 77 (65).

S-(4-Chlorophenyl) thiobenzoate 7f. From 4-chlorothiophenol (16%) as colourless crystals, mp 57–59 °C (HRMS: found M^+, 248.0057. $C_{13}H_9{}^{35}ClOS$ requires M, 248.0063); ν_{max}/cm^{-1} 1680; δ_H 8.0–8.15 (2 H, m) and 7.2–7.7 (7 H, m); δ_C 190.0 (C=O), 136.9 (2 C), 136.5 (*C*-Cl), 134.5, 130.1 (2 C), 129.9 (4ry), 129.4 (2 C), 128.1 (2 C) and 126.4 (4ry); *m/z* 250 (^{37}Cl-M^+, 3%), 248 (^{35}Cl-M^+, 10), 226 (4), 198 (2), 176 (4), 145 (6,), 143 (18), 122, (6), 105 (100), 91 (75) and 77 (92).

Preparation of substituted benzophenones. These were prepared by Friedel–Crafts acylation of benzene with the appropriate substituted benzoyl chloride in the presence of aluminium chloride.

4-Methylbenzophenone 9e. Yellow solid (52%), mp 49–50 °C (lit.,[21] 50–51 °C); δ_H 7.7–7.9 (4 H, m), 7.4–7.6 (3 H, m), 7.2–7.3 (2 H, m) and 2.43 (3 H, s); δ_C 196.3 (C=O), 143.2 (*C*-Me), 137.9 (4ry), 134.9 (4ry), 132.1, 130.2 (2 C), 129.9 (2 C), 128.9 (2 C), 128.2 (2 C) and 21.6.

4-Chlorobenzophenone 9f. Off-white solid (84%), mp 72–73 °C (lit.,[22] 75.5–76 °C); δ_H 7.7–7.8 (4 H, m) and 7.4–7.7 (5 H, m); δ_C 195.4 (C=O), 138.9 (C–Cl), 137.2 (4ry), 135.9 (4ry), 132.6, 131.4 (2 C), 129.9 (2 C), 128.6 (2 C) and 128.4 (2 C).

Preparation of thiobenzophenones 8. These were prepared according to the method of Gattermann[23] by reaction of the corresponding benzophenone **9** with an excess of phosphorus pentasulfide in boiling xylene followed by evaporation and distillation.

Thiobenzophenone 8d. Blue liquid (69%), bp 170 °C (oven temp.) at 0.1 Torr (lit.,[24] 174 °C at 14 Torr) (HRMS: found, M^+, 198.0541. $C_{13}H_{10}S$ requires M, 198.0503); λ_{max}/nm 570; δ_H 7.25–7.85 (10 H, m); δ_C 238.3 (C=S), 147.2 (2 C, 4ry), 131.9 (2 C), 129.6 (4 C) and 127.9 (4 C).

4-Methylthiobenzophenone 8e. Blue liquid (37%), bp 170 °C (oven temp.) at 0.1 Torr (lit.,[25] 136–138 °C at 0.3 Torr) (HRMS: found M^+, 212.0648. $C_{14}H_{12}S$ requires M, 212.0660); λ_{max}/nm 585; δ_H 7.1–7.8 (9 H, m) and 2.38 (3 H, s); δ_C 237.7 (C=S), 147.6

(4ry), 144.8 (4ry), 143.1 (4ry), 131.7, 129.9 (2 C), 129.5 (2 C), 128.7 (2 C), 127.9 (2 C) and 21.6.

4-Chlorothiobenzophenone 8f. Blue liquid (20%), bp 170 °C (oven temp.) at 0.1 Torr (lit.,[25] 145–146 °C at 0.22 Torr) (HRMS: found M^+, 232.0102. $C_{13}H_9{}^{35}ClS$ requires M, 232.0113); ν_{max}/nm 592; δ_H 7.2–7.8 (10 H, m); δ_C 236.2 (C=S), 146.9 (4ry), 145.3 (4ry), 138.5 (4ry), 132.1, 130.8 (2 C), 129.4 (2 C), 128.2 (2 C) and 128.0 (2 C).

Acknowledgements

References

1 Part 12, R. A. Aitken, M. J. Drysdale, G. Ferguson and A. J. Lough, *J. Chem. Soc.*, *Perkin Trans. 1*, 1998, 875.
2 For a recent review see: R. A. Aitken and A. W. Thomas, in *Chemistry of the Functional Groups*, *Supplement A3*, ed. S. Patai, Wiley, Chichester, 1997, p. 503.
3 A. M. Van Leusen, A. J. W. Iedema and J. Strating, *J. Chem. Soc.*, *Chem. Commun.*, 1968, 440.
4 L. Horner and H. Oediger, *Chem. Ber.*, 1958, **91**, 437; S. Trippett and D. M. Walker, *J. Chem. Soc.*, 1959, 3874.
5 Preliminary communication, R. A. Aitken, M. J. Drysdale and B. M. Ryan, *J. Chem. Soc.*, *Chem. Commun.*, 1993, 1699.
6 A. M. Hamid and S. Trippett, *J. Chem. Soc. C*, 1968, 1612; A. D. Josey, USP 3 647 856/1972 (*Chem. Abstr.*, 1972, **76**, 141023).
7 M. Mikolajczyk, W. Perlikowska, J. Omelanczuk, H.-J. Cristeau and A. Perraud-Darcy, *Synlett*, 1991, 913; H.-J. Cristeau, A. Perraud, E. Manginot and E. Torreiles, *Phosphorus Sulfur Silicon Relat. Elem.*, 1993, **75**, 7.
8 J.-H. Youn and R. Herrmann, *Synthesis*, 1987, 72.
9 C. G. Venier, H. J. Barager III and M. A. Ward, *J. Am. Chem. Soc.*, 1975, **97**, 3238; K. Schank, in *Houben-Weyl Methoden der Organischen Chemie*, 4th edn., Vol. E19b, ed. M. Regitz, Thieme, Stuttgart, 1989, p. 1713.
10 D. Hodson and G. Holt, *J. Chem. Soc.* (*C*), 1968, 1602.
11 C. F. Ebbinghaus, P. Morrissey and R. L. Rosati, *J. Org. Chem.*, 1979, **44**, 4697.
12 P. E. O'Bannon and W. P. Dailey, *Tetrahedron Lett.*, 1988, **29**, 987, 5719.
13 D. Frank, G. Himbert and M. Regitz, *Chem. Ber.*, 1978, **111**, 183.
14 M. Franck-Neumann and J. J. Lohmann, *Tetrahedron Lett.*, 1979, 2397.
15 R. L. Rosati, L. V. Kapili, P. Morrissey, J. Bordner and E. Subramanian, *J. Am. Chem. Soc.*, 1982, **104**, 4262.
16 A. R. Maguire, P. G. Kelleher and S. E. Lawrence, *Tetrahedron Lett.*, 1998, **39**, 3849.
17 M. Mikolajczyk, University of Lodz, personal communication.
18 R. A. Aitken and J. I. Atherton, *J. Chem. Soc.*, *Perkin Trans. 1*, 1994, 1281.
19 R. Otto and R. Lüders, *Ber. Dtsch. Chem. Ges.*, 1880, **13**, 1283.
20 R. Schiller and R. Otto, *Ber. Dtsch. Chem. Ges.*, 1876, **9**, 1634.
21 E. Ador and A. A. Rillet, *Ber. Dtsch. Chem. Ges.*, 1879, **12**, 2298.
22 M. Kollarits and V. Mertz, *Ber. Dtsch. Chem. Ges.*, 1873, **6**, 563.
23 L. Gatterman, *Ber. Dtsch. Chem. Ges.*, 1895, **28**, 2877.
24 B. F. Gofton and E. A. Braude, *Org. Synth.*, 1955, **35**, 98.
25 H. Tokunaga, K. Akiba and N. Inamoto, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 506.

Paper 8/06182C